

AMS-C14 analysis of graphite obtained with an Automated Graphitization Equipment (AGE III) from aerosol collected on quartz filters

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ABSTRACT

AMS- ^{14}C applications often require the analysis of small samples. Such is the case of atmospheric aerosols where frequently only a small amount of sample is available. The ion beam physics group at the ETH, Zurich, has designed an Automated Graphitization Equipment (AGE III) for routine graphite production for AMS analysis from organic samples of approximately 1 mg. In this study, we explore the potential use of the AGE III for graphitization of particulate carbon collected in quartz filters. In order to test the methodology, samples of reference materials and blanks with different sizes were prepared in the AGE III and the graphite was analyzed in a MICADAS AMS (ETH) system. The graphite samples prepared in the AGE III showed recovery yields higher than 80% and reproducible ^{14}C values for masses ranging from 50 to 300 μg . Also, reproducible radiocarbon values were obtained for aerosol filters of small sizes that had been graphitized in the AGE III. As a study case, the tested methodology was applied to PM₁₀ samples collected in two urban cities in Mexico in order to compare the source apportionment of biomass and fossil fuel combustion. The obtained ^{14}C data showed that carbonaceous aerosols from Mexico City have much lower biogenic signature than the smaller city of Cuernavaca.

1. INTRODUCTION

The presence of particulate matter in the atmosphere has severe effects in health [1,2], visibility [3], climate [4] and ecosystems [5,6]. It is one of the major concerns in environmental public policies. Aerosol pollution is frequently measured through PM₁₀ and PM_{2.5} (particulate matter with aerodynamical diameter lower than 10 microns and 2.5 microns respectively). Particulate carbonaceous matter (black carbon and organic carbon) is found to constitute one-fifth to one-half the annual average of PM_{2.5} throughout North America [7]. In Mexico City geological material was the largest PM₁₀ component accounting 38–58% of measured mass, whereas organics were the second-largest components, accounting for 18–33% of PM₁₀ [8–13]. The chemical composition PM is complex; data from PM composition are generally used in chemical mass balance models, which combine similar data sets from many source types to calculate the contribution of each source to ambient pollution [11]. A recent study reports a contribution of food cooking to PM_{2.5} of about 10% (5 μgm^{-3}), which would represent about 20% of the organic aerosols, although this study was not able to separately quantify biomass burning and the authors suggest that that problem may have inflated the contribution of other sources [13]. But recent studies have shown that radiocarbon content of the carbonaceous fraction collected in filters can be used to estimate the relative contribution of biomass and fossil-fuel sources of pollution, ^{14}C analysis is now being used routinely [14–16]. Biomass burning (BB), such as domestic biofuel combustion (stoves for cooking and heating etc.), agricultural burning (crop residues, leaves), and wildfires, is an important source of carbonaceous aerosols that scatter and absorb incident solar radiation, thereby affecting the Earth's albedo as well as causing visibility impairment [9,10,17–19]. ^{14}C analysis are expensive; however most of the proposed modern carbon tracers of BB such as levoglucosane, may not be used in a quantitative way, since they are highly dependent on combustion conditions or the presence of inorganic ions, therefore ^{14}C used in combination with other organic tracers, may be considered as a suitable alternative; nevertheless, a limiting factor for the measurement is the low sample size implied in analysis [20]. The Environmental Radionuclides Group of the University of Bern and the group of AMS at ETH Zurich has approached this issue by a direct AMS analysis of gaseous CO_2 samples. The CO_2 is obtained from the combustion of particulate matter on quartz filters, then, the gas is directly introduced into the AMS through a Gas Injection System (GIS) developed at ETH Zurich [21]. Since most AMS laboratories use graphite to analyze ^{14}C and only a few have a GIS system, this way to analyze small samples is not widespread yet. In order to obtain the graphite for radiocarbon analysis, the ETH group also developed computer controlled graphitization equipment named AGE III. It is coupled to an elemental analysis system (EA) Vario Micro Cube from Elementar. In this system seven carbonaceous samples (that can be of diverse nature origin such as wood, coal, collagen, vegetable fibers, etc.) can be graphitized in two simple steps, the first of combustion, the second of graphitization, without using vacuum lines or liquid nitrogen. The organic sample (regularly of 1 mg) is combusted in the elemental analyzer and the CO_2 produced is transferred by the He carrier gas into the graphitization unit where carbon is converted to graphite through the reduction by hydrogen over iron as catalyst [22]. In order to extend the use of the AGE III to graphitize particulate carbon in aerosol filters, whose carbon content may be in range of tenths of milligram/cm², we tested the graphitization methodology for samples as low as 50 micrograms of the standard reference material NIST 4990C Oxalic acid II (OXA II) and ^{14}C free blanks. Then, we compared filters graphitization in the AGE III and with different ^{14}C carbon contents in order to test the reproducibility. This methodology was finally applied to determine and compare the ^{14}C content in atmospheric aerosols (PM₁₀) collected (during November and December 2012) in two Mexican cities with very different anthropogenic activities: Mexico City and Cuernavaca, with nearly 20 million and 1.8 million inhabitants respectively. The data

obtained in this study will contribute to the knowledge of aerosols chemistry and sources of particulate carbon in this region.

2. METHODS

2.1. Aerosol filters collection

In order to test the reproducibility, radiocarbon analyses were carried out in on four aerosol quartz filters and their duplicates provided by Dr. Szidat. Details on the procedures for aerosols collection by his group can be seen elsewhere [27]. For the Mexican case study, coarse PM10 aerosols from Mexico and Cuernavaca were collected in quartz filters exposed for 48 h, using a high-volume air sampler (Graseby Andersen SA-2000H) at flow rate of 1.5 L min^{-1} , between 21 November and 6 December 2012 (dry and cold season). This sampling season was chosen for its light winds and low or no precipitation.

The sampling in Mexico City was performed in downtown, at the Automated Atmospheric Monitoring Network of Mexico City (RAMA). Aerosols were also sampled in Cuernavaca; a city located 80 km South Mexico City. PM10 collectors were located a residential site near the highway to Mexico City.

2.2. CO₂ extraction, purification and RC analysis of particulate carbon in filters

In order to obtain a homogeneous sample of the collected aerosol, a circular hole of 6 mm diameter was cut out from each filter. Samples sizes ranging from a carbon total mass of 100–250 μg were converted to graphite in the AGE III as previously described. AMS analyses were performed in a MICADAS system of the ETH at Zurich. Data reduction was performed with BATS, the computer program with the MICADAS [28], using also small OXAI standards and phthalic acid ($\text{C}_8\text{H}_6\text{O}_4$) blanks for normalization and background correction. The ^{14}C results are expressed as a fraction of modern Carbon (F^{14}C) that represents the $^{14}\text{C}/^{12}\text{C}$ ratio of the sample related to the isotopic ratio in 1950.

2.3. Graphite yield

In order to quantify the graphite yield obtained in the AGEIII, a series of graphite samples of different sizes from 1 mg down to 50 μg of carbon were obtained from an OXA II standard. The volume of the reactors plays an important role in the preparation of small samples [23,24] but given the relatively small volume of the AGE III reactors ($\sim 2.9 \text{ cm}^3$ approximately), the original volume was not modified. Since the water removal is a critical step when small samples are prepared [25], the yield of the combustion and graphitization processes was tested using three methods of water removal: Peltier cooled by air (0°C), Peltier cooled by water ($\sim 25^\circ\text{C}$) and by chemical absorption with Magnesium perchlorate ($\text{Mg}(\text{ClO}_4)_2$) [26]. Samples were reduced in reactors at 580°C for 140 min (for large and small samples) in the presence of H_2 ($\text{PH}_2/\text{PCO}_2 = 2.3$). Iron (Alfa-Aesar 325 mesh) was used as catalyst and the amount was kept constant (4.8–5.2 mg) regardless the carbon sample size.

Yield was calculated using the following expression:

$$\text{Graphite yield} = (\text{P}(\text{CO}_2 + \text{H}_2)_{\text{initial}} - \text{P}(\text{CO}_2 + \text{H}_2)_{\text{final}}) / 3\text{P}(\text{CO}_2)_{\text{initial}}$$

where P is the pressure in the reactors and 3CO_2 corresponds to the theoretical pressure of a 100% reaction ($\text{PH}_2/\text{PCO}_2 = 2.3$) [24].

3. RESULTS AND DISCUSSION

Small samples of OXAI standard were graphitized in the AGE III trapping the water produced during the reaction using several methods: the first experiments were performed comparing cryogenic retention with Peltiers cooled by air (0°C) and chemical absorption with magnesium perchlorate ($\text{Mg}(\text{ClO}_4)_2$). Fig. 1 shows the ^{14}C counts for graphite targets processed by each method. It can be seen that in general more CO_2 reacted with perchlorate than with air cooling. Peltiers cooled by water were set up later as another approach for trapping the water produced in the graphitization reaction. Table 1 shows the ^{12}C currents at the accelerator of samples processed using the three methods to retain the water formed during graphitization. Higher currents were obtained when water was trapped by Peltiers cooled by water ($\sim 25^\circ\text{C}$) or with $\text{Mg}(\text{ClO}_4)_2$ than when water was trapped with Peltiers cooled by air. After that, the yield of the combustion and graphitization processes was tested for different sample mass using $\text{Mg}(\text{ClO}_4)_2$ as a water trap. Results for graphite yield are shown in Table 2 for samples with different carbon contents. Graphite yield was around 80% for $50\text{ }\mu\text{g}$ samples and slightly higher for larger ones. Fig. 2 shows the Fraction modern carbon ($F^{14}\text{C}$) obtained for of OXA II standard run with standards and blanks of similar sizes. Obtained results are similar to the nominal value, regardless the sample size. More scattering is observed at lower sample sizes, but it decreases as one approach higher carbon masses (close to $1000\text{ }\mu\text{g}$). The effect of the phthalic acid (blank) size on $F^{14}\text{C}$ values is shown in Table 3. The reproducibility of the radiocarbon values was tested for aerosol filters containing different carbon masses, around $100\text{ }\mu\text{g}$. Similar values were obtained for two replicates, as is shown in Table 4.

An apportionment study based on radiocarbon analyses of aerosol filters using the tested methodology for small samples was finally applied to a case study in Mexico: values for the fraction of modern carbon ($F^{14}\text{C}$) obtained from the ^{14}C analysis of total carbon in aerosols (PM10 fraction), collected in Mexico City and Cuernavaca are shown in Fig. 3. Fossil fuels have no ^{14}C content ($F^{14}\text{C}$ equals zero), while carbon from modern sources show a $F^{14}\text{C}$ close or higher than one, due to the increase of ^{14}C in the atmosphere after the nuclear bomb tests in the 1950's. After 1963, atmospheric nuclear tests decreased resulting in lower ^{14}C release. Values of $F^{14}\text{C}$ ranged from 0.39 to 0.47 with an average of 0.43 in Mexico City. These results were slightly lower than those reported for PM2.5 collected in Mexico in March 2006 during the MILAGRO campaign [29], but higher than those reported a year later by a different group [30]. Our data show that an important apportionment from modern carbon aerosol sources in Mexico City can still be detected, in spite of the continuous growth of the vehicular fleet. This result can be due to a more stringent regulation and better vehicular technologies. A temporal effect was observed in Mexico City, where the highest value was observed on 25 November, a Sunday. Cuernavaca City had higher $F^{14}\text{C}$ values ranging from 0.65 to 0.68 with an average of 0.66. The results show that Cuernavaca is less affected by the traffic emissions and the relative contribution of modern sources of ^{14}C is more important. Cuernavaca city showed only minor variations on $F^{14}\text{C}$ over the course of the measurement.

4. CONCLUSIONS

We were able to prepare graphite targets in the AGEIII and perform AMS ^{14}C analysis of small samples down to 50 μg of OXAI standard with a good carbon recovery factor (higher than 80%), as graphite and with $\delta^{14}\text{C}$ similar to the nominal standard value. Beam currents on the AMS system depends on sample size, but using standards and blanks of similar carbon mass, as well as a background correction for contamination, allowed us to obtain reliable $^{14}\text{C}/^{12}\text{C}$ ratios and therefore accurate $\delta^{14}\text{C}$ regardless the sample size.

Radiocarbon analysis performed with filters graphitized in the AGE III gave reproducible results, showing that sample preparation with this equipment is reliable for source apportionment studies as well as other studies where high precision is required and where sample sizes are low.

The method was applied to a case study in two cities of Mexico with different anthropogenic activities in order to explore the apportionment of non-fossil sources. Mexico City fraction of modern carbon $\delta^{14}\text{C}$ was 0.43 in average while Cuernavaca had an average $\delta^{14}\text{C}$ of 0.66.

Although the impact of the non-fossil sources is observed in both cities, the contribution of biogenic sources is more evident in Cuernavaca. This result is not surprising since Cuernavaca has fewer inhabitants (almost 10 times) than Mexico City.

Average $\delta^{14}\text{C}$ values of total Carbon measured in filters collected for this study in Mexico City are close to values obtained in the MILAGRO campaign carried out in 2006. In spite of the continuous growth of the population and vehicular fleet, the impact of the modern carbon sources has remained almost constant. This result may be due to more stringent environmental regulations and better vehicle technologies. A next step should include a longer and wider study of Mexican cities coupled with the measurement of specific markers of the modern and fossil particulate carbon in aerosol filters.

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Table 1

Comparison of the performances of the AGE III with three methods for trapping the water produced during the graphitization of OXA II standards and blanks (n is the number of analyzed filters, the ^{12}C current is the mean of at least 20 measurements, a single measurement corresponds to 10 cycles of 30 s each).

Carbon average mass (μg)	Water trapping	^{12}C current (μA)	<i>n</i>
71	$\text{Mg}(\text{ClO}_4)_2$	1.3 ± 0.2	4
70	Water	1.2 ± 0.2	4
67	Air	0.8 ± 0.2	6
122	$\text{Mg}(\text{ClO}_4)_2$	1.6 ± 0.9	2
117	Water	1.7 ± 0.6	2
117	Air	1.2 ± 0.4	3

Table 2

Graphite yield using $\text{Mg}(\text{ClO}_4)_2$ for water absorption at different carbon contents of standard or filters. Yield was calculated using the Eq. (1). $\text{H}_2/\text{CO}_2 = 2.3$ (n is the number of analyzed samples, SD is the mass or yield standard deviation).

n	Carbon mass (μg)	SD	Yield (%)	SD
2	55	6	80	3
3	70	4	79	3
3	100	2	87	7
2	130	2	93	5
2	180	8	92	2
2	200	4	90	4
4	245	6	89	4
3	272	8	82	4
7	670	5	92	2

Table 3

F¹⁴C of blank material (Phthalic acid C₈H₆O₄) at different carbon masses (n is the number of analyzed samples).

<i>n</i>	Carbon mass (μg)	F ¹⁴ C graphite	Error (%)
2	100	0.0034	9
2	250	0.0016	13
2	400	0.0014	11
2	1000	0.0005	21

Table 4

F¹⁴C determination of aerosol filters of varying ¹⁴C contents graphitized in the AGEIII and their corresponding duplicates.

Sample ID	F ¹⁴ C graphite	δ ¹³ C (‰)	Weight (μg of C)
ETH-46494.1.1	0.18 ± 0.02	−18.0	67
ETH-46494.1.2	0.19 ± 0.02	−22.6	116
ETH-46495.1.1	0.44 ± 0.01	−20.7	102
ETH-46495.1.2	0.44 ± 0.01	−22.4	100
ETH-46496.1.1	0.58 ± 0.01	−20.3	101
ETH-46496.1.2	0.57 ± 0.01	−24.7	97
ETH-46497.1.1	0.82 ± 0.01	−23.5	117
ETH-46497.1.2	0.81 ± 0.01	−22.1	126

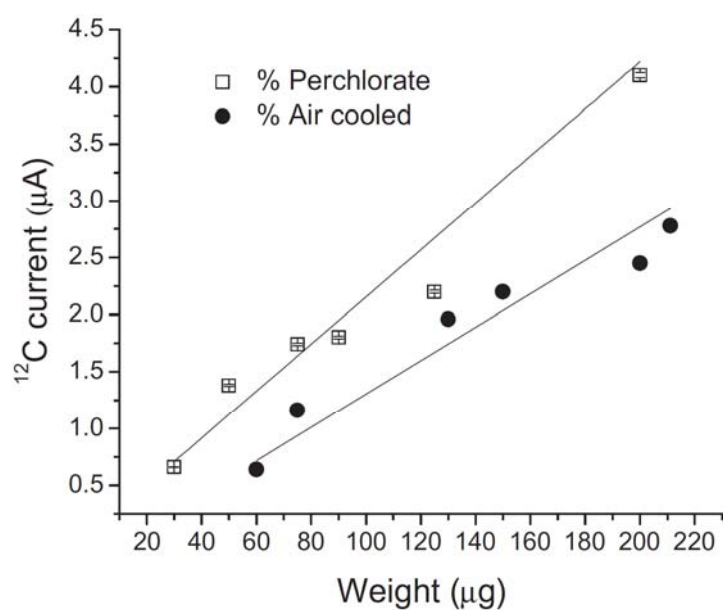
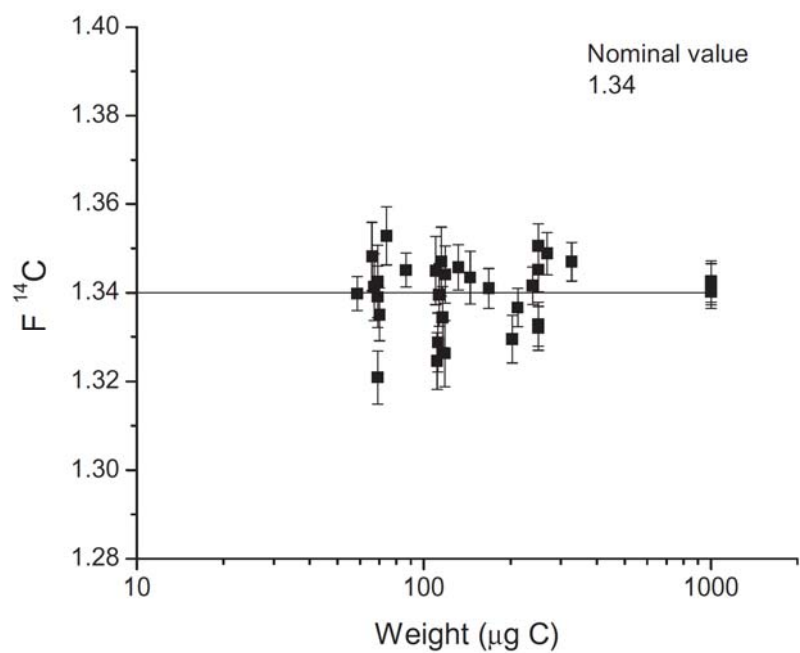


Fig. 1.

Comparison of the ^{12}C currents at different sample masses of OXA II standard when water is retained with Peltier coolers and Magnesium Perchlorate.



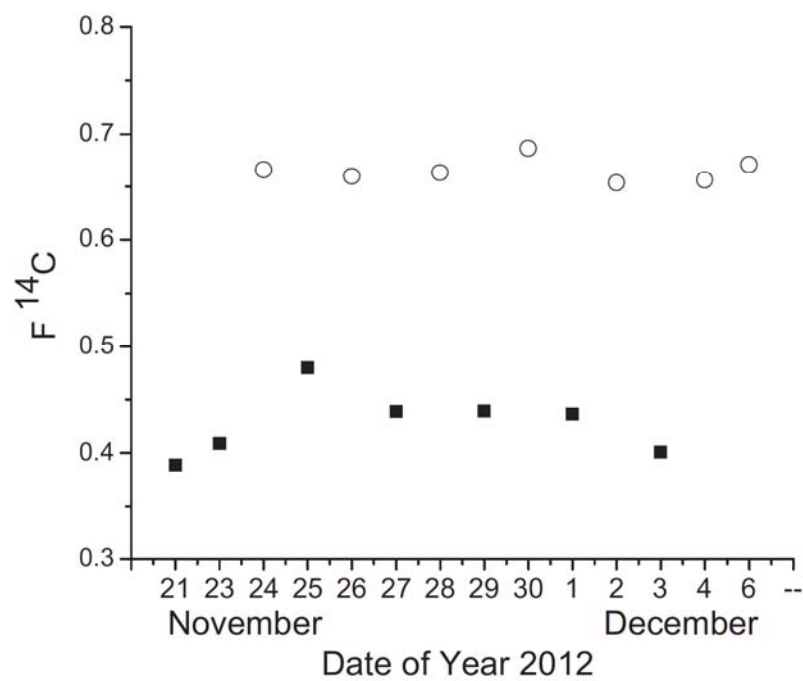


Fig. 3.

Fraction of modern carbon ($F^{14}C$) in PM10 aerosol samples collected in Mexico City (bottom) and Cuernavaca (top) in November and December 2012.